Polymerisation of Indole. Part 3.[1] Two Indolylquinolines, an Indole Tetramer, and the Dihydro Derivative of the Indole Dimer

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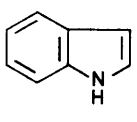
Treatment of indole (**1**) with toluene-*p*-sulphonic acid in Dowtherm A gave the dihydro dimer (**7**), the indol-3-ylquinoline (**8**), the indol-2-ylquinoline (**10**), and the tetramer (**19**). The indol-3-ylquinoline (**8**) was also produced on treatment of the 2,3′-trimer (**3**) with zinc chloride in acetic acid or with toluene-*p*-sulphonic acid in Dowtherm A. The identification of these products (**7**), (**8**), (**10**), and (**19**) is described and the mechanisms of formation are discussed.

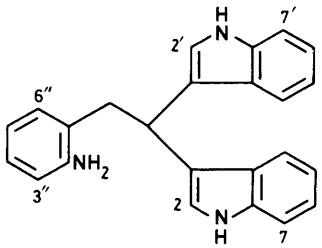
In the preceding paper,[1] we reported the formation of a new indole trimer, 2,3′-(*o*-aminophenethylidene)di-indole (the 2,3′-trimer) (**3**), on treatment of indole (**1**) with toluene-*p*-sulphonic acid in benzene, although it is well known that treatment of indole (1) under various acid conditions gave 3-(indolin-2-yl)-indole[2] (the dimer) (**6**) and/or 3,3′-(*o*-aminophenethylidene)di-indole[2] (the 3,3′-trimer) (**2**). The formation of the 2,3′-trimer (**3**) was explainable in terms of a Plancher rearrangement[3] of the 3,3′-trimer (**2**). However, there was a question as to why a second Plancher rearrangement did not take place, with the 2,3′-trimer (**3**). During studies on this subject, we occasionally found that indole (**1**) provided four new polymeric products, 2-(*o*-aminobenzyl)-3-(indol-3-yl)quinoline (the indol-3-ylquinoline) (**8**), 2-(*o*-aminobenzyl)-3-(indol-2-yl)quinoline (the indol-2-ylquinoline) (**10**), 6,12-bis(*o*-aminobenzyl)indolo-[3,2-*b*]carbazole (the tetramer) (**19**), and 3-(*o*-aminophenethyl)-indole (the dihydro dimer) (**7**), under several sets of acid conditions. In this report, we describe the identification of these products and discuss their mechanism of formation.

Initially, the 2,3′-trimer (**3**) was treated with zinc chloride in acetic acid at room temperature for 32 h to give the indol-3-ylquinoline (**8**), m.p. 168—170 °C, in 39.4% yield, as sole product. The molecular formula $C_{24}H_{19}N_3$ was established by elemental analysis. In the desorption/chemical ionisation mass spectrum,[4] with isobutane as reagent gas, the protonated molecule ion (MH^+) was clearly observed at *m/z* 350, as a base peak, showing that the indol-3-ylquinoline (**8**) is an oxidation product of the starting 2,3′-trimer ($C_{24}H_{21}N_3$) (**3**). The i.r. spectrum shows three NH bands at 3 430, 3 320, and 3 200 cm^{-1}, and the ^1H n.m.r. spectrum (270 MHz; $CDCl_3$) shows broad singlets ascribable to NH protons at δ 8.36 (1 H) and 4.90 (2 H) and twelve aromatic proton signals [set *a* (δ 7.45, 7.17, 7.30, and 7.51), set *b* (δ 6.57, 6.88, 6.37, and 6.19), and set *c* (δ 7.76, 7.50, 7.69, and 8.06)] (Table 1), together with a benzylic methylene signal at δ 4.26 and two further aromatic proton signals at δ 7.13 (1 H, d, *J* 2.6 Hz), and 8.09 (1 H, s).

Treatment of the indol-3-ylquinoline (**8**) with acetic anhydride gave a monoacetyl derivative (**9**). The i.r. spectrum



(**1**)



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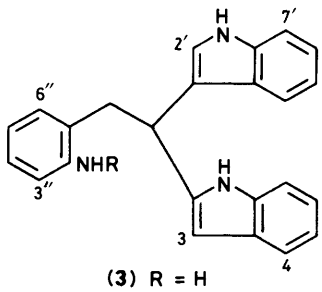
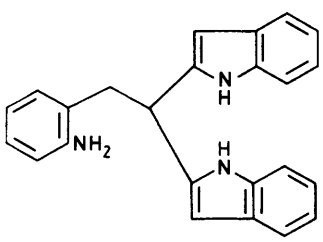
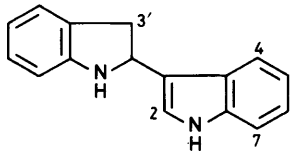


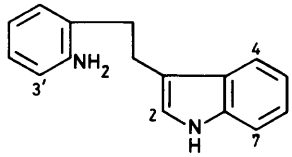
(**3**) R = H
(**4**) R = Ac



(**5**)



(**6**)



(**7**)

Table 1. ^{1}H N.m.r. signals (270 MHz; $CDCl_3$) (δ values; *J* in Hz) of the indolylquinoline derivatives (**8**)—(**11**)

		(**8**)	(**9**)	(**10**)	(**11**)
Indolic H		8.36 (1 H, br s)	8.52 (1 H, br s)	8.19 (1 H, br s)	8.33 (1 H, br s)
	2′-H	7.13* (1 H, d, *J* 2.6)	7.18* (1 H, d, *J* 2.6)		
	3′-H			6.72* (1 H, diffuse d, *J* 1.7)	6.73* (1 H, d, *J* 1.7)
Set a	4′-H	7.45 (1 H, diffuse d, *J* 7.5)	7.40 (1 H, br d, *J* 7.7)	7.71 (1 H, d, *J* 7.5)	7.75 (1 H, d, *J* 7.6)
	5′-H	7.17 (1 H, diffuse t, *J* 7.5)	7.19 (1 H, diffuse t, *J* 7.7)	7.19 (1 H, diffuse d, *J* 7.5)	7.23 (1 H, d, *J* 7.6)
	6′-H	7.30 (1 H, dt, *J* 7.5, 1.0)	7.33 (1 H, dt, *J* 7.7, 1.1)	7.26 (1 H, diffuse d, *J* 7.5)	7.30 (1 H, diffuse t, *J* 7.6)
	7′-H	7.51 (1 H, diffuse d, *J* 7.5)	7.56 (1 H, d, *J* 7.7)	7.38 (1 H, diffuse d, *J* 7.5)	7.45 (1 H, d, *J* 7.6)
	CH_2	4.26 (2 H, s)	4.32 (2 H, s)	4.35 (2 H, s)	4.43 (2 H, s)
	$COCH_3$		2.47 (3 H, s)		2.40 (3 H, s)
	NH	4.90 (2 H, br s)	11.36 (1 H, br s)	4.82 (2 H, br s)	11.04 (1 H, br s)
Set b	3-H	6.57 (1 H, dd, *J* 7.6, 1.3)	7.99 (1 H, br d, *J* 7.7)	6.64 (1 H, d, *J* 6.5)	7.97 (1 H, d, *J* 8.0)
	4-H	6.88 (1 H, dt, *J* 7.6, 1.3)	7.10 (1 H, dt, *J* 7.7, 1.3)	6.99 (1 H, m)	7.08 (1 H, diffuse t, *J* 8.0)
	5-H	6.37 (1 H, dt, *J* 7.6, 1.3)	6.71 (1 H, dt, *J* 7.7, 1.3)	6.50 (1 H, diffuse t, *J* 6.5)	6.77 (1 H, t, *J* 8.0)
	6-H	6.19 (1 H, dd, *J* 7.6, 1.3)	6.32 (1 H, diffuse d, *J* 7.7)	6.54 (1 H, d, *J* 6.5)	6.59 (1 H, dd, *J* 8.0, 0.9)
	4″-H	8.09 (1 H, s)	8.13 (1 H, s)	8.20 (1 H, s)	8.21 (1 H, s)
Set c	5″-H	7.76 (1 H, br d, *J* 7.7)	7.79 (1 H, br d, *J* 7.9)	7.80 (1 H, d, *J* 8.2)	7.82 (1 H, d, *J* 7.6)
	6″-H	7.50 (1 H, diffuse t, *J* 7.7)	7.54 (1 H, diffuse t, *J* 7.9)	7.54 (1 H, diffuse t, *J* 8.2)	7.57 (1 H, t, *J* 7.6)
	7″-H	7.69 (1 H, dt, *J* 7.7, 1.3)	7.74 (1 H, dt, *J* 7.9, 1.5)	7.73 (1 H, diffuse t, *J* 8.2)	7.78 (1 H, diffuse t, *J* 7.6)
	8″-H	8.06 (1 H, br d, *J* 7.7)	8.04 (1 H, d, *J* 7.9)	8.06 (1 H, d, *J* 8.2)	8.03 (1 H, d, *J* 7.6)

* Signal changed from a doublet to a singlet on addition of deuterium oxide.

shows an amide absorption at 1 680 cm^{-1} and the ^{1}H n.m.r. spectrum (270 MHz; $CDCl_3$) exhibits a new NAc singlet at δ 2.47 and two broad NH singlets at δ 8.52 and 11.36. All other signals of the acetamide (**9**) can be correlated with those of the indol-3-ylquinoline (**8**).

Comparison of the signals of the acetamide (**9**) with those of the starting indol-3-ylquinoline (**8**) established the structure of compound (**8**). The doublet (*J* 2.6 Hz) at δ 7.13 or 7.18 in (**8**) or (**9**), respectively, changed to a singlet on addition of deuterium oxide, suggesting the existence of an indole nucleus: this behaviour[1,5] of the signal due to the 3-H or 2-H of indole derivatives is well known. Furthermore, the indol-3-ylquinoline (**8**) shows a double doublet at δ 6.57 (*J* 7.6 and 1.3 Hz), but the corresponding signal of the *N*-acetyl derivative (**9**) is shifted to δ 7.99, as a broad doublet (*J* 7.7 Hz). Such a large shift of only one aromatic proton signal on *N*-acetylation is explainable if the indol-3-ylquinoline (**8**) contains an *ortho*-substituted aniline moiety. Since this material (**8**) was produced from the 2,3′-trimer (**3**), the foregoing deduction implied the presence of an indol-3-yl- (**8**) or indol-2-yl- (**10**) quinoline.

In order to provide conclusive proof, oxidative cleavage of the pyrrole ring of the indole portion of the acetamide (**9**) was attempted. Treatment with 10.3% trifluoroperacetic acid in trifluoroacetic acid gave the desired cleavage product (**12**), but oxidation was not achieved with chromium trioxide,[6] sodium metaperiodate[7] in tetrahydrofuran, periodic acid[7] in dioxane, or 30% hydrogen peroxide[8] in acetic acid. In the ^{1}H and ^{13}C n.m.r. spectra, the cleavage product (**12**) shows signals attributable to a formyl function at δ_H 8.64 and δ_C 159.9.

The cleavage product (**12**) was easily hydrolysed under acidic or basic conditions to give the corresponding amino ketone (**13**). This allowed us to identify the new product as the indol-3-ylquinoline (**8**).

The formation of the indol-3-ylquinoline (**8**) from the 2,3′-trimer (**3**) is easily explicable in terms of the following steps: (i) protonation at C-3 of the 2,3′-trimer (**3**) to give an indolium ion (**15**); (ii) attack of the amino group of the aniline portion on C-2 to give a cyclisation product (**17**); (iii) the cleavage of the 1,2-bond of the spiro-indoline moiety of the cyclisation product (**17**) to produce the 3,4-dihydroquinoline derivative (**18**); and (iv) finally, oxidation of the 3,4-dihydroquinoline (**18**) by air to give the indol-3-ylquinoline (**8**). This mechanism probably explains why Plancher rearrangement of the 2,3′-trimer (**3**) does not take place. Protonation at the C-3 or -3′ of the 2,3′-trimer (**3**) gives two different indolium cations, (**15**) and (**16**), but the former (**15**) would be formed in preference to the latter (**16**) because a trisubstituted iminium cation would be expected to be more stable than a disubstituted one. Thus, the re-cyclisation of

the 2,3′-trimer (**3**) to the indol-3-ylquinoline (**8**) is preferred to a second Plancher rearrangement.

Treatment of the 2,3′-trimer (**3**) with anhydrous zinc chloride in acetic acid under reflux gave a mixture of indole (**1**), the indol-3-ylquinoline acetate (**9**), and the 2,3′-trimer monoacetate[1] (**4**) in 9.8, 17.0, and 40.4% yield, respectively.

The foregoing experimental results stimulated us to find conditions under which indole (**1**) itself gives the indol-3-ylquinoline (**8**) directly. Preliminary tests on polymerisation of indole (**1**) with toluene-*p*-sulphonic acid or trifluoromethanesulphonic acid in benzene and Dowtherm A[9] were evaluated by t.l.c. (Table 2).

Treatment of indole (**1**) with toluene-*p*-sulphonic acid in Dowtherm A gave the desired indol-3-ylquinoline (**8**) along with three new polymers: the dihydro dimer (**7**), the indol-2-ylquinoline (**10**), and the tetramer (**19**), in 22.2, 1.1, 0.57, and 6.0% yield, respectively. The dihydro dimer (**7**) was not detected in the preliminary test, because it shows very weak colouration on t.l.c.

The molecular formula, $C_{16}H_{16}N_2$, was established for the dihydro dimer (**7**) on the basis of elemental analysis and mass spectral measurement. In the ^{1}H n.m.r. spectrum (270 MHz; $CDCl_3$), it shows a broad NH singlet at δ 7.92, and four aromatic proton signals (δ 7.62, 7.12, 7.20, and 7.36), sequentially arranged, together with an aromatic doublet (1 H, *J* 2.3 Hz) at δ 6.95. The last signal changed to a singlet on addition of deuterium oxide, suggesting the presence of a 3-substituted indole skeleton.

Moreover, the appearance of two two-proton multiplets due to aliphatic protons at δ 2.90 and 3.10 and a two-proton broad singlet due to NH at δ 3.60, along with a further set of four aromatic signals (δ 7.10, 6.75, 7.05, and 6.67), also arranged sequentially, indicated the existence of a 2-substituted aniline moiety.

As this spectral evidence was in accord with structure (**7**) for the dihydro dimer, hydrogenolysis of the dimer (**6**) was examined. Catalytic hydrogenation over 10% palladium–charcoal in acetic acid at room temperature for 25 h gave the dihydro dimer (**7**) in 25.2% yield. This was identical with the product (**7**) already obtained.

The presence of such a reduction product (**7**) in the reaction mixture suggests that disproportionation of the dimer (**6**) with the resulting 3,4-dihydroquinoline derivative (**18**) takes place in the polymerisation of indole (**1**) under the strongly acidic conditions. However, oxidation by air must be another important factor for formation of the oxidation products such as the indol-3- and -2-ylquinolines (**8**) and (**10**) and the tetramer (**19**), because the yield of the dihydro dimer (**7**) was too low to explain formation of all of them.

The molecular formula of the indol-2-ylquinoline (**10**), $C_{24}H_{19}N_3$, was established on the basis of elemental analysis and mass spectral measurement, suggesting that it was a structural isomer of the indol-3-ylquinoline (**8**). Acetylation gave a monoacetate (**11**) under the similar conditions as applied to the indol-3-ylquinoline (**8**). Comparison of the ^{1}H n.m.r. spectra (270 MHz; $CDCl_3$) of the indol-2-ylquinoline (**10**) with that of the indol-3-ylquinoline (**8**) gave structural proof for the former (Table 1). In the ^{1}H n.m.r. spectrum, all signals of the indol-2-ylquinoline (**10**) were easily correlated with those of the indol-3-ylquinoline (**8**), except for two one-proton aromatic signals at δ 6.72 (diffuse, *J* 1.7 Hz) and 7.71 (d, *J* 7.5 Hz). The fact that the diffuse doublet at δ 6.72 changed to a diffuse singlet on addition of deuterium oxide allowed us to assign this signal to a proton at a pyrrole ring of the indole moiety. This assignment obliged us to conclude that the signal at δ 7.71 is due to 4′-H. Since the structure of the indol-3-ylquinoline (**8**) was well established chemically, these spectral data provided definitive evidence for the indol-2-ylquinoline (**10**).

This finding prompted us to examine whether Plancher rearrangement of the indol-3-ylquinoline (**8**) to the indol-2-ylquinoline (**10**) would take place. Treatment of the former (**8**) with toluene-*p*-sulphonic acid in Dowtherm A under the same conditions as used in the case of indole (**1**) itself resulted only in recovery of the starting material (**8**).

However, similar treatment of the 2,3′-trimer (**3**) gave the starting material (**3**), the indol-3-ylquinoline (**8**), the indol-2-ylquinoline (**10**), and the tetramer (**19**) in 11.0, 34.3, 0.30, and 0.04%, yields, respectively. It is of interest that the indol-2-

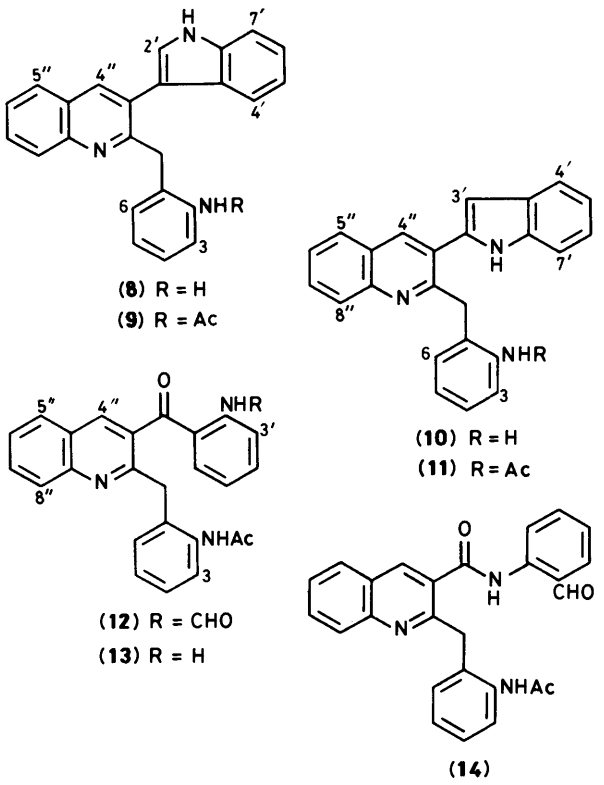
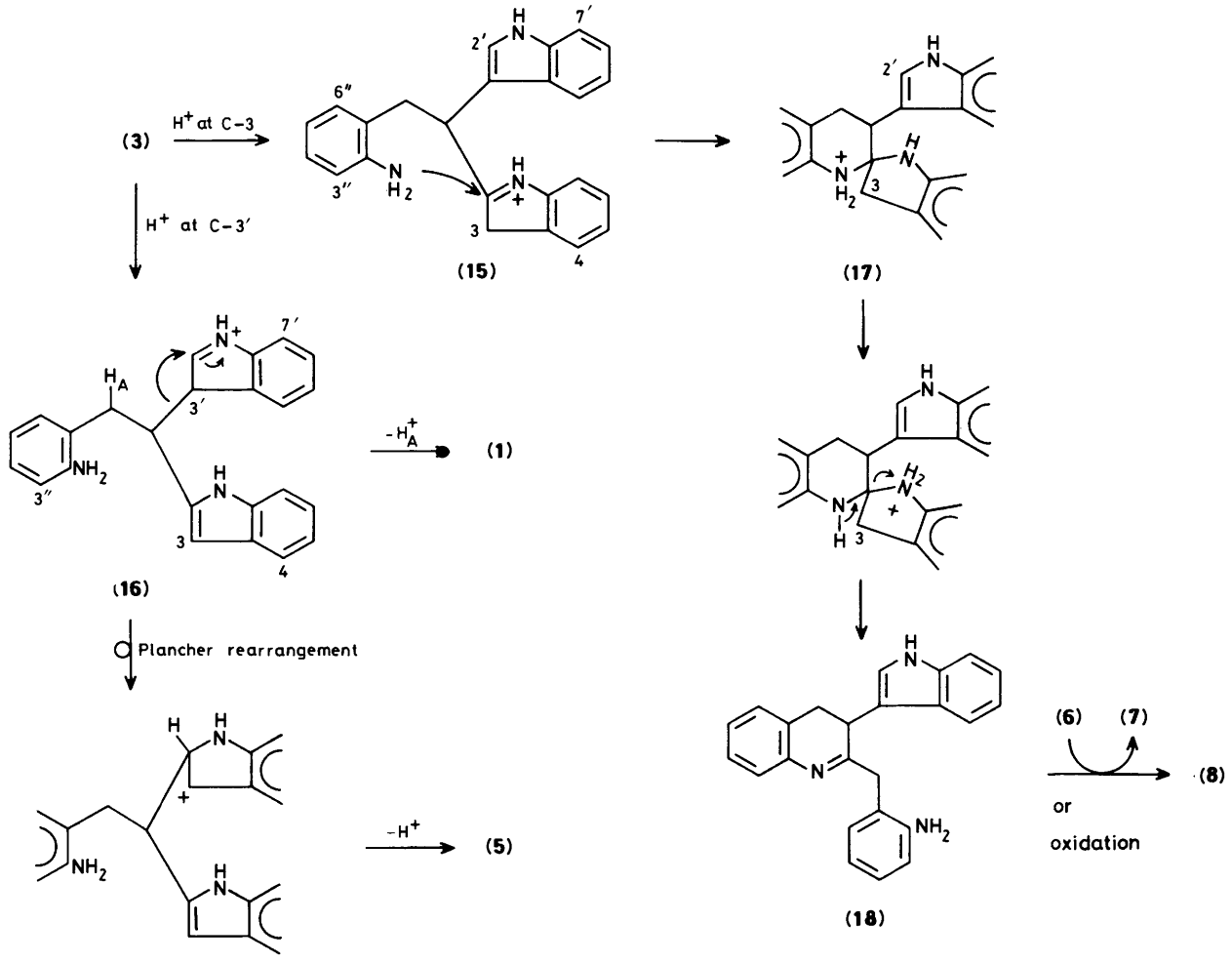
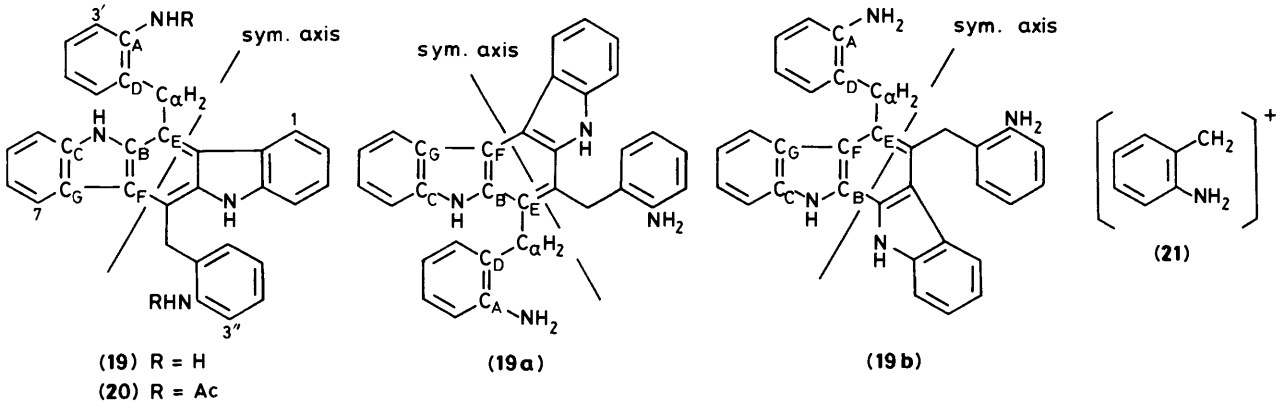


Table 2. Preliminary tests for polymerisation of indole (**1**) under various acid conditions by monitoring on t.l.c.

		Products						
	Conditions	Indol-3-yl-quinoline (**8**)	Indol-2-yl-quinoline (**10**)	Tetramer (**19**)	2,3′-Trimer (**3**)	3,3′-Trimer (**2**)	Dimer (**6**)	Recovered indole (**1**)
CF_3SO_3H, PhH	Reflux, 3.5 h	+	−	+	++	±	±	+++
CF_3SO_3H, Dowtherm A	110 °C, 4.5 h	+++	−	+	±	±	−	++
TsOH, Dowtherm A	110 °C, 5 h	+++	±	+	±	−	−	+



Scheme 1.



ylquinoline (**10**) was formed in this reaction, although the Plancher rearrangement of the indol-3-ylquinoline (**8**) to the indol-2-ylquinoline (**10**) does not proceed. This fact may be explained by supposing that protonation at C-3′ of the 2,3′-trimer (**3**) took place to some extent, and a minute amount of the postulated 2,2′-trimer (**5**) was formed by the second Plancher rearrangement. The intramolecular recyclisation of the 2,2′-trimer (**5**) gave the indol-2-ylquinoline (**10**).

The tetramer (**19**) was obtained as a relatively labile product, $C_{32}H_{26}N_4$ (tentatively established on the basis of elemental analyses and mass spectral measurement). Acetylation gave a diacetate (**20**), which was so labile that all attempts at detailed characterisation failed. In the ^{1}H n.m.r. spectrum [270 MHz; $(CD_3)_2SO$], the tetramer (**19**) shows only thirteen protons, ascribable to a benzylic group [ArCH_2Ar: δ 4.62 (2 H, s)], two types of NH function [δ 5.39 (2 H, s) and 11.11 (1 H, s)], and two sets of four aromatic protons [set *a* (δ 6.23, 6.18, 6.87, and 6.80) and set *b* (δ 7.41, 7.27, 6.93, and 7.72)]. The ^{13}C n.m.r. spectrum shows only sixteen signals, ascribable to one methylene carbon atom (δ 29.2), eight unsubstituted aromatic carbon atoms (δ 110.2, 114.2, 115.9, 117.4, 121.9, 124.6, 126.3, and 126.5), and seven substituted aromatic carbon atoms (δ 112.2, 120.7, 122.4,

122.7, 135.4, 141.2, and 146.3). The fact that the numbers of observed signals due to protons and carbon atoms in both n.m.r. spectra are half of those of the molecular formula means that the tetramer (**19**) must have an entirely symmetric structure. In the mass spectrum, the tetramer (**19**) shows the fragment $C_7H_8N^+$, corresponding to an aminobenzyl cation (**21**). These spectral data allow only three possible structures (**19**), (**19a**), and (**19b**) for the tetramer.

In order to choose the correct structure, ^{13}C-{^1H} long-range selective proton decoupling (LSPD) experiments [270 MHz; $(CD_3)_2SO$] on the tetramer (**19**) were carried out. Of the signals due to seven quaternary carbon atoms, the lowest three [δ 135.4 (dt, *J* 4.5 and 4.5 Hz), 141.2 (dt, *J* 8.2 and 1.6 Hz), and 146.3 (br t, *J* 7.1 Hz)] were assignable to the carbon atoms A—C adjacent to nitrogen. Irradiation at δ_H 11.11, corresponding to the indolic NH proton, changed the signals at δ_C 135.4 and 141.2 to triplets (*J* 4.5 and 7.1 Hz), but not the signal at δ_C 146.3. On the other hand, irradiation at δ_H 4.62, corresponding to the α-protons, converted the signals at δ_C 135.4 and 146.3 to a doublet (*J* 4.5 Hz) and a sharp triplet (*J* 8.2 Hz), respectively, but did not affect the signal at δ_C 141.2. These spectral data indicate the following facts: (i) the carbon atom corresponding to δ_C 135.4 should be within the γ-positions of both the indolic NH and the C_α-protons; (ii) the carbon atom corresponding to δ_C 141.2 is situated within the γ-position of the former, but outside the γ-position of the latter; and (iii) the carbon atom corresponding to δ_C 146.3 is in the converse situation. These deductions led us to exclude structure (**19b**) and to assign the signals at δ_C 135.4, 141.2, and 146.3 to carbon atoms B, C, and A, respectively. The validity of these assignments was confirmed by H–H and C–H correlation spectroscopy* (COSY) and H–H long-range COSY* (COSYLR) on the tetramer (**19**).

Although some fragmentary information on assignments of signals for the tetramer (**19**) were obtained from the LSPD experiments, no conclusive evidence enabling a choice to be made between structures (**19**) and (**19a**) was found. A correlation spectroscopy *via* long-range coupling (COLOC) experiment*[10] was therefore carried out. This clearly showed long-

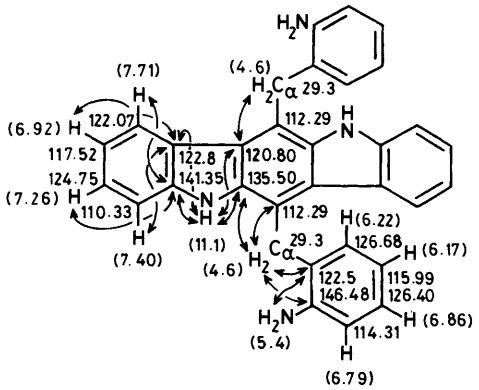
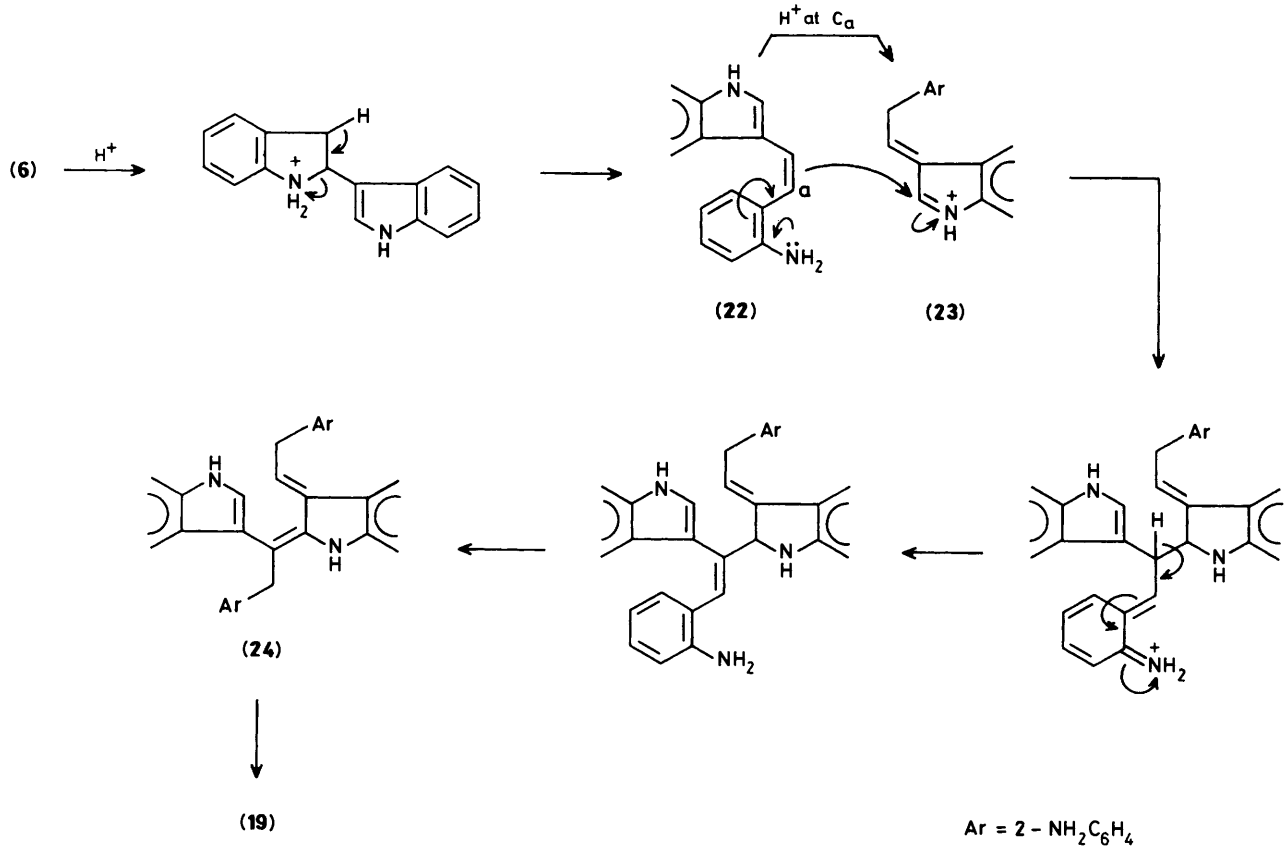
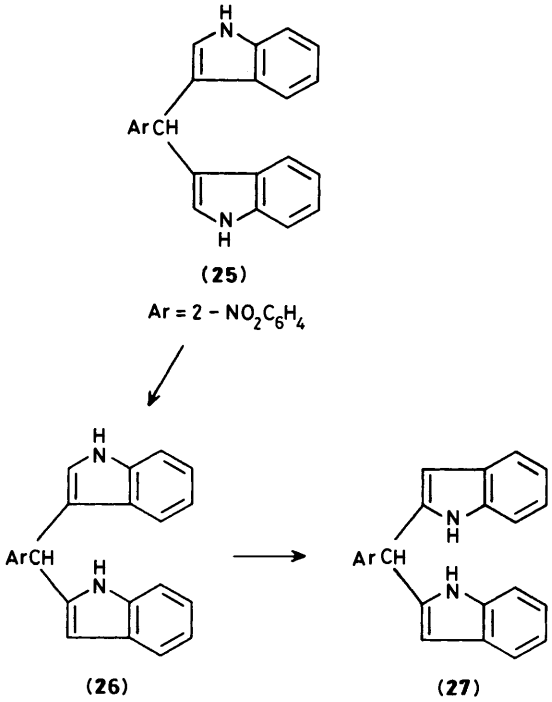


Figure. Results of the C–H correlations with the tetramer (**19**) determined by the COLOC method {^{13}C n.m.r. [$(CD_3)_2SO$]; ^1H n.m.r. [$(CD_3)_2SO$] in parentheses}

* This experiment was performed with a Bruker AM 400 wb {^1H n.m.r. [400 MHz; $(CD_3)_2SO$] and ^{13}C n.m.r. [100.62 MHz; $(CD_3)_2SO$]} spectrometer. The data are slightly different from those obtained with a JEOL-JNM-FX-270 instrument (270 MHz for ^1H n.m.r. and 67.8 MHz for ^{13}C n.m.r.), but within experimental error. An incredible natural abundance double quantum transfer experiment (INADEQUATE) was also tried. However, the solubility in $(CD_3)_2SO$ was not enough to obtain a definitive result, and the substrate (**19**) decomposed when heated at 40 °C.



Scheme 2.



Scheme 3.

range coupling between the C_α-protons (δ_H 4.6) and the carbon atom F (δ_C 120.80). This fact is explainable by the structure (**19**) but not (**19a**), because carbon atom F must be located nearer than the γ-position with respect to the C_α-protons (Figure).

We believe that the tetramer (**19**) is produced by dimerisation of the dimer (**6**) by a pathway including electrocyclic cyclisation of the intermediate (**24**) followed by oxidation (Scheme 2). Treatment of indole (**1**) itself with toluene-*p*-sulphonic acid in Dowtherm A gave the tetramer (**19**) in 6.0% yield. From the 2,3′-trimer (**3**), the tetramer was formed in extremely low yield (0.04%) and in the case of the indol-3-ylquinoline (**8**), starting material was recovered quantitatively. Formation of a trace of the tetramer (**19**) from the 2,3′-trimer (**3**) might be explained if we suppose that a small amount of indole (**1**) is produced from the cation (**16**) under acidic conditions through the pathway shown in Scheme 1.

In view of this deduction, we wondered if the formation of the tetramer (**19**) had been overlooked in a previous experiment.[1] We therefore re-examined the polymerisation of the indole (**1**) with toluene-*p*-sulphonic acid in benzene, in place of Dowtherm A, and recognized that the tetramer (**19**) was actually produced in 4.8% yield.

Finally, all attempts failed to synthesize 2,2′-(*o*-nitrophenethylidene)di-indole (**27**) from 3,3′-(*o*-nitrophenethylidene)di-indole[1] (**25**) *via* 2,3′-(*o*-nitrophenethylidene)di-indole (**26**) (Scheme 3).

Experimental

M.p.s were measured with a micro hot stage (Yanagimoto). I.r. spectra were recorded for Nujol mulls with Hitachi EPI-G3 and Hitachi 215 spectrometers. U.v. spectra were recorded for solutions in 95% ethanol with a Hitachi 340 spectrometer. N.m.r. spectra (^1H and ^{13}C) were recorded with a JEOL-JNM-FX-270 instrument (270 MHz for ^1H and 67.8 MHz for ^{13}C), with tetramethylsilane as internal reference. The correlation spectroscopy *via* long-range coupling (COLOC) experiment was performed with a Bruker AM 400 wb {^1H [400 MHz; $(CD_3)_2SO$] and ^{13}C [100.62 MHz; $(CD_3)_2SO$]} spectrometer. Assignments for those signals due to NH and indolic 2-H and 3-H marked with an asterisk were confirmed by their behaviour on additon of D_2O (disappearance of the NH signal and a change of a doublet to a singlet for 2-H and 3-H). For chromatography, silica gel 60 (70—230 mesh ASTM; Merck) and aluminium oxide 90 (70—230 mesh, Aktivitätsstufe II–III; Merck) were used; for t.l.c. and preparative t.l.c., silica gel GF_{254} (Merck) was used. Products were identified by i.r. spectroscopy, mixed m.p., and t.l.c.

Treatment of the 2,3′-Trimer (**3**) *with Zinc Chloride in Acetic Acid at Room Temperature; 2-(o-Aminobenzyl)-3-(indol-3-yl-quinoline* (**8**).—A solution of the 2,3′-trimer (**3**) (0.043 g) and freshly prepared anhydrous zinc chloride (0.019 g) in acetic acid (1.4 ml) was stirred at room temprature† for 32 h. The mixture was poured into a large quantity of water, made alkaline with aqueous 10% sodium hydroxide, and extracted with chloroform. The chloroform solution was dried (K_2CO_3) and evaporated to dryness under reduced pressure. Preparative t.l.c. with diethyl ether–hexane (3:1 v/v) gave colourless *needles* (0.017 g), m.p. 168—170 °C (from methylene dichloride–diethyl ether) (Found: C, 81.9; H, 5.6; N, 11.8. $C_{24}H_{19}N_3 \cdot \frac{1}{6}H_2O$ requires C, 81.8; H, 5.5; N, 11.9%); $\nu_{max.}$ 3 430, 3 320, and 3 200 cm^{-1}; $\lambda_{max.}$ 222, 272, 290sh, 318sh, and 336 nm (log ε 4.85, 4.23, 4.13, 3.65, and 3.61); for $\delta_H(CDCl_3)$ see Table 1; δ_H [$(CD_3)_2SO$] 3.47* (1 H, br s, NH), 4.22 (2 H, s, CH_2), 5.32* (1 H, br s, NH), 6.11 (1 H, d, *J* 7.4 Hz, 6-H), 6.26 (1 H, t, J 7.4 Hz, 5-H), 6.62 (1 H, d, *J* 7.4 Hz, 3-H), 6.83 (1 H, diffuse t, *J* 7.4 Hz, 4-H), 7.10 (1 H, t, *J* 7.6 Hz, 5′-H), 7.22 (1 H, t, *J* 7.6 Hz, 6′-H), 7.39* (1 H, d, *J* 2.0 Hz, 2′-H), 7.50 (1 H, d, *J* 7.6 Hz, 4′-H), 7.55 (1 H, d, *J* 7.6 Hz, 7′-H), 7.57 (1 H, t, *J* 8.0 Hz, 6″-H), 7.73 (1 H, t, *J* 8.0 Hz, 7″-H), 7.99 (1 H, d, *J* 8.0 Hz, 5″-H), 8.02 (1 H, d, *J* 8.0 Hz, 8″-H), 8.33 (1 H, s, 4″-H), and 11.48* (1 H, d, *J* 2.0 Hz, NH); δ_C [$(CD_3)_2SO$] 38.5 (t, CH_2), 111.9 (d, C-7′), 112.8 (s, C-3′), 114.8 (d, C-3), 115.8 (d, C-5), 118.6 (d, C-4′), 119.6 (d, C-5′), 121.5 (d, C-6′), 123.3 (s, C-1), 124.8 (d, C-2′), 126.1 (d, C-6″), 126.6 (s), 126.7 (s), 126.7 (d, C-4), 127.5 (d, C-5″), 127.9 (d, C-8″), 128.9 (s), 129.1 (d, C-6 and -7″), 136.0 (s, C-7′a), 137.2 (d, C-4″), 145.6 (s, C-2 or -8″a), 146.6 (s, C-8″a or -2), and 160.0 (s, C-2″); *m/z* 350 (M^+ + 1, 30.6%), 349 (M^+, 100), 348 (M^+ − 1, 47.1), 334 (64.5), and 255 (26.4) (Found: M^+, 349.1571. $C_{24}H_{19}N_3$ requires *M*, 349.1577); *m/z* [isobutane chemical ionisation (c.i.)] 350 (M^+H, 100%).

Acetylation of the Indol-3-ylquinoline (**8**).—A suspension of the indol-3-ylquinoline (**8**) (0.698 g) in acetic anhydride (2.5 ml) was stirred at room temperature for 20 min, poured onto a large quantity of ice–water, made alkaline with sodium hydrogen carbonate, and extracted with chloroform. The chloroform solution was dried (K_2CO_3) and evaporated to dryness under reduced pressure. Recrystallisation from chloroform–methanol gave colourless needles of the acetyl derivative (**9**) (0.719 g), m.p. 250—253 °C (Found: C, 79.4; H, 5.3; N, 10.6. $C_{26}H_{21}N_3O$ requires C, 79.8; H, 5.4; N, 10.7%); $\nu_{max.}$ 3 225 and 1 680 cm^{-1}; $\lambda_{max.}$ 221, 270, 288sh, 318sh, and 340 nm (log ε 4.86, 4.24, 4.11, 3.58, and 3.58); for $\delta_H(CDCl_3)$ see Table 1; δ_H[$(CD_3)_2SO$] 2.20 (3 H, s, COMe), 4.40 (2 H, s, CH_2), 6.44 (1 H, d, *J* 7.5 Hz, 6-H), 6.81 (1 H, t, *J* 7.5 Hz, 5-H), 7.10 (2 H, t, *J* 7.5 Hz, 4- and 5′-H), 7.23 (1 H, t, *J* 7.5 Hz, 6′-H), 7.46 (1 H, d, *J* 7.5 Hz, 4′-H), 7.47* (1 H, diffuse s, 2′-H), 7.57 (1 H, d, *J* 7.5 Hz, 7′-H), 7.59 (1 H, t, *J* 7.8 Hz, 6″-H), 7.69 (1 H, d, *J* 7.5 Hz, 3-H), 7.77 (1 H, t, *J* 7.8 Hz, 7″-H), 8.00 (1 H, d, *J* 7.8 Hz, 5″-H), 8.03 (1 H, d, *J* 7.8 Hz, 8″-H), 8.36 (1 H, s, 4″-H), 10.42* (1 H, s, NH), and 11.51* (1 H, s, NH); δ_C [$(CD_3)_2SO$] 23.9 (q, Me), 38.0 (t, CH_2), 111.8 (d, C-7′), 112.5 (s, C-3′), 118.4 (d, C-4′), 119.5 (d, C-5′), 121.5 (d, C-6′), 123.4 (d, C-3), 123.7 (d, C-5), 124.9 (d, C-2′), 126.3 (d, C-4 and -6″), 126.5 (s),

† If required, the mixture was heated at 50 °C.

126.7 (s), 127.5 (d, C-5″ and -8″), 128.7 (s), 129.3 (d, C-6 and -7″), 131.1 (s), 136.0 (s), 136.8 (s), 137.8 (d, C-4″), 145.4 (s, C-8″a), 160.1 (s, C-2″), and 167.8 (s, CO); *m/z* 391 (M^+, 100%).

2-(o-*Acetamidobenzyl*)-3-(o-*formamidobenzoyl*)*quinoline* (**12**).—The acetyl indol-3-ylquinoline (**9**) (0.047 g) was added to a mixed solution† of trifluoroacetic anhydride (0.52 ml) and 30% hydrogen peroxide (0.07 ml) cooled in ice. The mixture was stirred at 0 °C for 20 min,‡ poured onto ice–water, basified with saturated aqueous sodium hydrogen carbonate, and extracted with chloroform. The chloroform solution was dried (K_2CO_3) and evaporated to dryness under reduced pressure. Preparative t.l.c. of the residue with chloroform–methanol (25:1, v/v) gave colourless *prisms*§ (0.029 g), m.p. 207.5—209.5 °C (from methylene dichloride–diethyl ether) (Found: C, 73.5; H, 5.1; N, 9.8. $C_{26}H_{21}N_3O_3$ requires C, 73.7; H, 5.0; N, 9.9%); $\nu_{max.}$ 3 300, 1 700, and 1 685 cm^{-1}; $\nu_{max.}$($CHCl_3$) 3 270 and 1 700 cm^{-1}; $\lambda_{max.}$ 232, 276sh, 323, and 348sh nm (log ε 4.70, 4.23, 3.83, and 3.64); δ_H 2.38 (3 H, s, COMe), 4.39 (2 H, s, CH_2), 6.79 (1 H, t, *J* 7.9 Hz, 5-H), 6.96 (1 H, t, *J* 7.9 Hz, 5′-H), 6.97 (1 H, d, *J* 7.9 Hz, 6-H), 7.13 (1 H, t, *J* 7.9 Hz, 4-H), 7.14 (1 H, d, *J* 7.9 Hz, 6′-H), 7.62 (2 H, t, *J* 7.9 Hz), 6″- and 4′-H), 7.81 (1 H, d, *J* 7.9 Hz, 5″-H), 7.85 (1 H, t, *J* 7.9 Hz, 7″-H), 8.01 (1 H, d, *J* 7.9 Hz, 3-H), 8.06 (1 H, s, 4″-H), 8.07 (1 H, d, *J* 7.9 Hz, 8″-H), 8.64 (1 H, br s, CHO), 8.82 (1 H, d, *J* 7.9 Hz, 3′-H), 10.58* (1 H, br s, NH), and 11.29* (1 H, br s, NH); δ_C 24.9 (q, Me), 39.2 (t, CH_2), 121.9 (d, C-3′), 122.8 (s), 123.0 (d, C-3), 123.1 (d, C-5′), 124.0 (d, C-5), 125.3 (s), 127.7 (d, C-6″), 127.9 (d, C-4), 128.1 (s), 128.1 (d, C-8″), 128.4 (d, C-5″), 130.5 (d, C-6), 131.9 (d, C-7″), 132.7 (s), 134.5 (d, C-6′), 136.1 (d, C-4′), 137.5 (s), 137.7 (d, C-4″), 140.5 (s), 147.1 (s, C-8″a), 158.3 (s, C-2″), 159.9 (d, CHO), 168.5 (s, *C*OMe), and 200.1 (s, CO); *m/z* 424 (M^+ + 1, 9.3%), 423 (M^+, 26.7), 394 ($C_{25}H_{20}N_3O_2^+$, 46.5), 379 ($C_{25}H_{19}N_2O_2^+$, 54.7), and 275 ($C_{18}H_{15}N_2O$, 100).

Hydrolysis of the o-*Formamidobenzoylquinoline* (**12**); (2-o-*Acetamidobenzyl*)-3-(o-*aminobenzoyl*)*quinoline* (**13**).—(a) *Under acid conditions.* A solution of the *o*-formamidobenzoylquinoline (**12**) (0.034 g) in aqueous trifluoroacetic acid (CF_3CO_2H–H_2O 13:6, v/v) (1.0 ml) was stirred at room temperature overnight. The mixture was made alkaline with saturated aqueous sodium hydrogen carbonate and extracted with chloroform. The chloroform solution was dried (K_2CO_3) and evaporated to dryness under reduced pressure. Recrystallisation from methylene dichloride–diethyl ether gave yellow *prisms* (0.031 g), m.p. 289—300 °C¶ (decomp.) (Found: C, 75.6; H, 5.4; N, 10.5. $C_{25}H_{21}N_3O_2$ requires C, 75.9; H, 5.35; N, 10.6%); $\nu_{max.}$ 3 450, 3 330, and 1 695 cm^{-1}; $\lambda_{max.}$ 231, 272sh, 308, 322, and 388 nm (log ε 4.69, 4.14, 3.60, 3.62, and 3.86); δ_H 2.43 (3 H, s, Me), 4.31 (2 H, s, CH_2), 6.44 (1 H, diffuse t, *J* 7.9 Hz, 5′-H), 6.56* (2 H, s, NH_2), 6.79 (1 H, diffuse d, *J* 7.9 Hz, 3′-H), 6.81 (1 H, diffuse t, *J* 7.9 Hz, 5-H), 6.97 (1 H, diffuse d, *J* 7.9 Hz, 6-H), 7.01 (1 H, diffuse d, *J* 7.9 Hz, 6′-H), 7.13 (1 H, diffuse t, *J* 7.9 Hz, 4-H), 7.33 (1 H, diffuse t, *J* 7.9 Hz, 4′-H), 7.58 (1 H, diffuse t, *J* 7.9 Hz, 6″-H), 7.80 (1 H, diffuse t, *J* 7.9 Hz, 7″-H), 7.81 (1 H, diffuse d, *J* 7.9 Hz, 5″-H), 7.99 (1 H, d, *J* 7.9 Hz, 3-H), 8.04 (1 H, d, *J* 7.9 Hz, 8″-H), 8.06 (1 H, s, 4″-H), and 11.03* (1 H, s, NHCO); *m/z* 395 (M^+, 13.3%), 394 (M^+ − 1, 19.7), 352 (M^+ − COMe), and 247 ($C_{16}H_{11}N_2O^+$, 100).

(b) *Under basic conditions.* A solution of the *o*-formamidobenzoylquinoline (**12**) (0.013 g) in ethanol (1.5 ml) containing aqueous 10% sodium hydroxide (0.2 ml) was kept at room temperature for 30 min. After addition of water, the mixture was extracted with chloroform. The chloroform solution was dried (K_2CO_3) and evaporated to dryness under reduced pressure. Recrystallisation of the residue from methylene dichloride–diethyl ether gave the *o*-aminobenzoylquinoline (**13**) (0.012 g).

Treatment of the 2,3′-*Trimer* (**3**) *with Zinc Chloride in Acetic Acid under Reflux.*—A solution of the 2,3′-trimer (**3**) (0.300 g) and freshly prepared anhydrous zinc chloride (0.045 g) in acetic acid (6 ml) was refluxed for 7.5 h. The mixture was poured into a large quantity of water and made alkaline with aqueous 20% sodium hydroxide. The resulting precipitate was collected by filtration. The filtrate was extracted with chloroform. The chloroform solution was dried (K_2CO_3) and evaporated to dryness under reduced pressure. A mixture of the residue and the precipitate was chromatographed on silica gel with benzene–ethyl acetate (4:1, v/v) to give three fractions which were purified by preparative t.l.c. with diethyl ether–hexane (3:1, v/v). The least-polar fraction gave indole (**1**) (0.029 g). Recrystallisation of the middle fraction from chloroform–methanol gave colourless needles (0.057 g), m.p. 252—254.5 °C, identical with an authentic sample of the *N*-acetyl indol-3-ylquinoline (**9**). The most polar fraction gave the monoacetyl 2,3′-trimer (**4**) (0.135 g).

Treatment of Indole (**1**) *with Toluene*-p-*sulphonic Acid in Dowtherm A;*[9] 2-(o-*Aminobenzyl*)-3-(*indol*-2-*yl*)*quinoline* (**10**).—(a) *Small-scale experiment.* A solution of toluene-*p*-sulphonic acid monohydrate (4.00 g) in dry benzene (80 ml) was refluxed for *ca.* 1 h in a Dean-Stark apparatus. After removal of benzene by distillation, the residue and indole (**1**) (6.16 g) were dissolved in Dowtherm A[9] [biphenyl–diphenyl ether (26.5:73.5 w/w)] (80 ml). The mixture was heated at 110 °C for 7 h with stirring and made alkaline with aqueous 10% sodium hydroxide. The alkaline solution was extracted with chloroform containing a small quantity of methanol and then with ethyl acetate.

The ethyl acetate solution was dried ($MgSO_4$) and evaporated to dryness under reduced pressure. The residue was washed with hot acetone to give a pale brown powder [the crude tetramer (**19**)] (0.377 g), m.p. > 300 °C.

The chloroform solution was dried (K_2CO_3) and evaporated to dryness under reduced pressure. The oily residue was chromatographed on aluminium oxide with benzene. The first eluate contained Dowtherm A[9] and a small amount of indole (**1**).

The second eluate gave a deep green mass, which afforded colourless prisms [the dihydro dimer (**7**)] (0.66 g) on washing with diethyl ether, followed by recrystallisation from diethyl ether–hexane.

Further elution with benzene and with chloroform gave a tarry mass. The tarry mass was dissolved in large quantities of diethyl ether. Addition of the ethereal solution in limited quantities to 5% hydrochloric acid with vigorous stirring produced a tarry mass again. The mixture was separated into three fractions, 5% hydrochloric acid, the tarry mass, and an ethereal solution. The ethereal solution was discarded. The tarry mass was suspended in aqueous 10% sodium hydroxide and extracted with chloroform containing a small quantity of methanol. The organic layer was dried (K_2CO_3) and evaporated to dryness under reduced pressure. The residue was dissolved in a large quantity of diethyl ether again and treated as before. The same treatment was repeated several times, and the 5% hydrochloric acid solution were combined.

† This solution acts as 10.3% trifluoroperacetic acid in trifluoroacetic acid; an amount of trifluoroacetic anhydride equimolar to the amounts of hydrogen peroxide and water in commercial 30% hydrogen peroxide was used.

‡ If the reaction was quenched by aqueous sodium sulphite and stirred at room temperature overnight, the *o*-aminobenzoylquinoline (**13**), the hydrolysis product, was obtained.

§ Sometimes the compound was obtained as colourless needles, m.p. 177—180 °C ($\nu_{max.}$ 3 250, 1 700, and 1 680 cm^{-1}) by recrystallisation from methylene dichloride–diethyl ether. Dimorphism was confirmed by i.r. spectroscopy in chloroform and cross-seeding experiments.

¶ This material melted at 188—191 °C and crystallised again as colourless needles.

The combined solution was basified with aqueous 10% sodium hydroxide and extracted with diethyl ether. The ethereal solution was dried (K_2CO_3) and evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel with benzene. After elution with benzene, elution with benzene–ethyl acetate (10:1 v/v) gave a crystalline mass which was recrystallised from diethyl ether to provide colourless prisms [(the indol-3-ylquinoline (**8**)] (1.09 g).

Evaporation of the ethereal mother liquor gave a mixture of two components, which was fractionated by preparative t.l.c. with diethyl ether–hexane (3:1 v/v). Recrystallisation of the less polar portion from methylene dichloride gave colourless prisms [the indol-2-ylquinoline (**10**)] (0.035 g).

The more polar portion gave more of the indol-3-ylquinoline (**8**) (0.269 g; total yield 1.36 g).

(b) *Large-scale experiment.* As in the small-scale experiment, indole (**1**) (32.0 g) was treated with toluene-*p*-sulphonic acid monohydrate (20.8 g), dry benzene (250 ml), and Dowtherm A[9] (420 ml). The mixture was stored in a refrigerator overnight. The resulting tarry mixture was separated from Dowtherm A[9] by decantation and washed with hexane. The Dowtherm A solution and hexane washings were combined. The resulting tarry mixture was separated and combined with the previous tarry mixture. The mixed solution was diluted with large quantities of diethyl ether and washed with aqueous 5% sodium hydroxide. The ethereal solution was extracted with 5% hydrochloric acid and discarded. The 5% hydrochloric acid was added dropwise to a mixture of aqueous 5% sodium hydroxide and diethyl ether with stirring. The almost pure tetramer (**19**) (0.157 g) was obtained by separation of insoluble material during the foregoing operation followed by washing with acetone. The combined tarry mixture (50.58 g) was dissolved in diethyl ether. At this point, the tetramer (**19**) was also obtained as insoluble material (0.547 g; total yield 0.730 g).

The two ethereal solutions were added to a mixture of a large quantity of diethyl ether and 5% hydrochloric acid with vigorous stirring, to give three fractions [the ethereal solution (neutral fraction), 5% hydrochloric acid (basic fraction), and a tarry mass]. The tarry mass was suspended in aqueous 10% sodium hydroxide and extracted with chloroform containing a small quantity of methanol. The chloroform solution was dried (K_2CO_3) and evaporated to dryness under reduced pressure. The residue was dissolved in diethyl ether containing a small quantity of methanol. The ethereal solution was treated like the starting ethereal solution. The same treatment was repeated several times to give a tarry mass. The ethereal fractions and 5% hydrochloric acid fractions were combined, independently.

The combined 5% hydrochloric acid solution was basified with aqueous 10% sodium hydroxide and extracted with diethyl ether. The ethereal solution was dried (K_2CO_3) and evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel with benzene. After elution with benzene, elution with benzene–ethyl acetate (20:1, v/v) gave the dihydro dimer (**7**) (0.565 g). Further elution gave the indol-2-ylquinoline (**10**) (0.140 g), followed by the indol-3-ylquinoline (**8**) (3.90 g).

The ethereal solution was dried (K_2CO_3) and evaporated to dryness under reduced pressure. Chromatography of the residue on silica gel with benzene–ethyl acetate (20:1, v/v) additionally gave the indol-2-ylquinoline (**10**) (0.070 g; total yield 0.210 g) and the indol-3-ylquinoline (**8**) (0.063 g; total yield 3.96 g).

3-(o-*Aminophenethyl*)*indole* (the dihydro dimer) (**7**) formed colourless prisms, m.p. 120—122 °C (from diethyl ether) (Found: C, 81.2; H, 6.9; N, 11.8. $C_{16}H_{16}N_2$ requires C, 81.3; H, 6.8; N, 11.9%); $\nu_{max.}$ 3 400, 3 325, and 3 200 cm^{-1}; δ_H 2.86—2.95 (2 H, m, $ArCH_2CH_2$), 3.05—3.14 (2 H, m, CH_2CH_2-indolyl), 3.60* (2 H, br s, NH_2), 6.67 (1 H, d, *J* 7.6 Hz, 6′-H), 6.75 (1 H, diffuse t, *J* 7.6 Hz, 4′-H), 6.95* (1 H, d, *J* 2.3 Hz, 2-H), 7.05 (1 H, diffuse t, *J* 7.6 Hz, 5′-H), 7.10 (1 H, d, *J* 7.6 Hz, 3′-H), 7.12 (1 H, diffuse t, *J* 7.6 Hz, 5-H), 7.20 (1 H, diffuse t, *J* 7.6 Hz, 6-H), 7.36 (1 H, d, *J* 7.6 Hz, 7-H), 7.62 (1 H, d, *J* 7.6 Hz, 4-H), and 7.92* (1 H, br s, NH); *m/z* 236 (M^+, 30.8%) and 130 ($C_9H_8N^+$, 100).

Catalytic hydrogenation of the dimer (**6**). A solution of the dimer (**6**) (0.15 g) in acetic acid (2.0 ml) containing aqueous 1% palladium chloride[11] (0.6 ml) and Norit (0.055 g) was hydrogenated at atmospheric pressure and 20 °C for 25 h. The catalyst was filtered off, and the filtrate was made alkaline with aqueous 10% sodium hydroxide and extracted with chloroform. The chloroform solution was dried (K_2CO_2) and evaporated to dryness under reduced pressure. Preparative t.l.c. with diethyl ether–hexane (1:1, v/v) gave indole (**1**) (0.007 g), the starting dimer (**6**) (0.008 g), and colourless prisms (0.038 g), m.p. 120—122 °C (from methylene dichloride–diethyl ether), identical with a sample of the dihydro dimer (**7**).

2-(o-*Aminobenzyl*)-3-(*indol-2-yl*)*quinoline* (the indol-2-ylquinoline) (**10**) formed colourless prisms (from methylene dichloride–diethyl ether), m.p. 165—167 °C (Found: C, 82.6; H, 5.5; N, 12.0. $C_{24}H_{19}N_3$ requires C, 82.5; H, 5.5; N, 12.0%); $\nu_{max.}$ 3 360 and 3 300—3 100br cm^{-1}; $\lambda_{max.}$ 230, 287, 324sh, and 354sh nm (log ε 4.80, 4.30, 4.00, 3.24, and 3.85); for $\delta_H(CDCl_3)$ see Table 1; $\delta_H[(CD_3)_2SO]$ 4.38 (2 H, s, CH_2), 5.28* (2 H, br s, NH_2), 6.22 (1 H, d, *J* 7.1 Hz, 6-H), 6.25 (1 H, t, *J* 7.1 Hz, 5-H), 6.63* (1 H, s, 3′-H), 6.64 (1 H, d, *J* 7.1 Hz, 3-H), 6.84 (1 H, diffuse t, *J* 7.1 Hz, 4-H), 7.05 (1 H, t, *J* 7.6 Hz, 5′-H), 7.17 (1 H, t, *J* 7.6 Hz, 6′-H), 7.48 (1 H, d, *J* 7.6 Hz, 7′-H), 7.57 (1 H, d, *J* 7.6 Hz, 4′-H), 7.60 (1 H, t, *J* 7.9 Hz, 6″-H), 7.77 (1 H, t, *J* 7.9 Hz, 7″-H), 8.01 (2 H, d, *J* 7.9 Hz, 5″- and 8″-H), 8.47 (1 H, s, 4″-H), and 11.60* (1 H, s, NH); $\delta_C[(CD_3)_2SO]$ 38.7 (t, CH_2), 102.8 (d, C-3′), 111.5 (d, C-7′), 115.1 (d, C-3, 116.4 (d, C-5), 119.6 (d, C-5′), 120.4 (d, C-4′), 122.0 (d, C-6′), 123.2 (s, C-1), 126.5 (s), 126.9 (d, C-6″), 127.1 (d, C-4), 127.4 (s), 128.0 (d, C-5″ or -8″), 128.2 (d, C-8″ or -5″), 128.4 (s), 129.1 (d, C-6), 130.2 (d, C-7″), 135.2 (s, C-2′, or C-7′a), 136.9 (s, C-7′a or -2′), 137.2 (d, C-4″), 146.2 (s, C-2 or -8″a), 146.8 (s, C-8″a or -2), and 158.8 (s, C-2″); *m/z* 349 (M^+, 100%).

Acetylation of the indol-2-ylquinoline (**10**); 2-(o-*Acetamidobenzyl*)-3-(*indol-2-yl*)*quinoline* (**11**). A solution of the indol-2-ylquinoline (**10**) (0.048 g) in acetic anhydride (0.2 ml) was stirred at room temperature for 25 min. The mixture was poured onto a large quantity of ice–water, made alkaline with sodium hydrogen carbonate, and extracted with chloroform. The chloroform solution was dried (K_2CO_3) and evaporated to dryness under reduced pressure. Recrystallisation of the residue from ethyl acetate gave pale yellow prisms of the *acetyl derivative* (**11**) (0.048 g), m.p. 205—206.5 °C (Found: C, 79.7; H, 5.5; N, 10.7. $C_{26}H_{21}N_3O$ requires C, 79.8; H, 5.4; N, 10.7%); $\nu_{max.}$ 3 310, 3 170, and 1 685 cm^{-1}; $\lambda_{max.}$ 220sh, 232, 287, 310sh, 320sh, and 346 nm (log ε 4.77, 4.82, 4.27, 4.02, 3.98, and 3.81); for $\delta_H(CDCl_3)$ see Table 1; $\delta_H[(CD_3)_2SO]$ 2.15 (3 H, s, COMe), 4.56 (2 H, s, CH_2), 6.63 (1 H, d, *J* 7.5 Hz, 6-H), 6.64* (1 H, s, 3′-H), 6.86 (1 H, t, *J* 7.5 Hz, 5-H), 7.07 (1 H, t, 7.6 Hz, 5′-H), 7.13 (1 H, t, *J* 7.5 Hz, 4-H), 7.18 (1 H, t, *J* 7.6 Hz, 6′-H), 7.48 (1 H, d, *J* 7.6 Hz, 7′-H), 7.60 (1 H, d, *J* 7.6 Hz, 4′-H), 7.63 (1 H, d, *J* 7.5 Hz, 3-H), 7.64 (1 H, t, *J* 7.3 Hz, 6″-H), 7.80 (1 H, t, *J* 7.3 Hz, 7″-H), 8.02 (1 H, d, *J* 7.3 Hz, 5″- or 8″-H), 8.04 (1 H, d, *J* 7.3 Hz, 8″- or 5″-H), 8.54 (1 H, s, 4″-H), 10.13* (1 H, s, NH), and 11.62* (1 H, s, NH); $\delta_C[(CD_3)_2SO]$ 23.7 (q, Me), 38.1 (t, CH_2), 102.7 (d, C-3′), 111.2 (d, C-7′), 119.2 (d, C-5′), 120.1 (d, C-4′), 121.6 (d, C-6′), 124.0 (s, C-3), 124.1 (d, C-5), 126.1 (s), 126.4 (d, C-4), 126.7 (d, C-6″), 126.9 (s), 127.7 (d, C-5″ and -8″), 128.1 (s), 129.1 (d, C-6), 130.0 (d, C-7″), 131.4 (s), 134.6 (s), 136.6 (s), 137.2 (d, C-4″), 145.8 (s, C-8″a), 158.5 (s, C-2″), and 167.9 (s, CO); *m/z* 391 (M^+, 100%).

Treatment of the 2,3′-*Trimer* (**3**) *with Toluene*-p-*sulphonic Acid in Dowtherm A.*[9]—According to the procedure for the small-scale experiment with indole (**1**) itself and toluene-*p*-

sulphonic acid, a solution of the 2,3′-trimer (**3**) (3.00 g) in Dowtherm A[9] (40 ml) was treated with dry toluene-*p*-sulphonic acid [from its monohydrate (1.95 g)] in a Dean-Stark apparatus with dry benzene (40 ml). The tetramer (**19**) (0.001 g) was obtained by separation of insoluble material followed by washing with hot acetone. The recovered 2,3′-trimer (**3**) (0.329 g) was obtained from the neutral fraction and the indol-2-ylquinoline (**10**) (0.010 g) and the indol-3-ylquinoline (**8**) (1.02 g) from the basic fraction.

6,12-*Bis*(o-*aminobenzyl*)*indolo*[3,2-b]*carbazole* (the tetramer) (**19**) was recrystallised from a large quantity of acetone to give colourless prisms, m.p. >300 °C (Found: C, 80.75; H, 5.7; N, 11.6. $C_{32}H_{26}N_4 \cdot 0.5H_2O$ requires C, 80.8; H, 5.7; N, 11.8%); $\nu_{max.}$ 3 400 cm^{-1}; $\lambda_{max.}$(dioxane) 238, 255sh, 265, 280, 304sh, 318, 334, 383, and 403 nm (log ε 4.61, 4.51, 4.51, 4.75, 4.18, 4.48, 4.76, 3.82, and 3.92); $\delta_H[(CD_3)_2SO]$ 4.62 (4 H, s, CH_2 × 2), 5.39* (4 H, s, NH_2 × 2), 6.18 (2 H, diffuse t, *J* 7.6 Hz, 5′- and 5″-H), 6.23 (2 H, diffuse d, *J* 7.6 Hz, 6′- and 6″-H), 6.80 (2 H, d, *J* 7.6 Hz, 3′- and 3″-H), 6.87 (2 H, diffuse t, *J* 7.6 Hz, 4′- and 4″-H), 6.93 (2 H, t, *J* 7.7 Hz, 2- and 8-H), 7.27 (2 H, t, *J* 7.7 Hz, 3- and 9-H), 7.41 (2 H, d, *J* 7.7 Hz, 4- and 10-H), 7.72 (2 H, d, *J* 7.7 Hz, 1- and 7-H), and 11.11* (2 H, s, NH × 2); $\delta_C[(CD_3)_2SO]$ 29.2 (t, CH_2), 110.2 (d, C-4 and -10), 112.2 (s), 114.2 (d, C-3′ and -3″), 115.9 (d, C-5, and -5″), 117.4 (d, C-2 and -8), 120.7 (s), 121.9 (d, C-1 and -7), 122.4 (s), 122.7 (s), 124.6 (d, C-3 and -9), 126.3 (d, C-4′ and -4″), 126.5 (d, C-6′ and -6″), 135.4 (s, C-5a and -11a), 141.2 (s, C-4a and -10a), and 146.3 (s, C-2′ and -2″); *m/z* 467 (M^+ + 1, 33.9%), 466 (M^+, 94.2), and 360 ($C_{25}H_{18}N_3^+$, 100) (Found: M^+ 466.2161. $C_{32}H_{26}N_4$ requires *M*, 466.2156).

Acetylation of the Tetramer (**19**); 6,12-*Bis*(o-*acetamidobenzyl*)*indolo*[3,2-b]*carbazole* (**20**).—A suspension of the tetramer (**19**) (0.020 g) in acetic anhydride (0.2 ml) was stirred at room temperature for 20 min. The mixture was poured onto a large quantity of ice–water, made alkaline with sodium hydrogen carbonate, and extracted with chloroform. The chloroform solution was dried (K_2CO_3) and evaporated to dryness under reduced pressure to give material (0.021 g), m.p. >300 °C, which was so labile that all attempts at recrystallisation failed; $\nu_{max.}$ 3 320, 3 200, and 1 675 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 2.28 (6 H, s, COMe × 2), 4.86 (4 H, s, CH_2 × 2), 6.51 (2 H, diffuse d, *J* 7.5 Hz, 6′- and 6″-H), 6.80 (2 H, diffuse t, *J* 7.5 Hz, 5′- and 5″-H), 6.94 (2 H, diffuse t, *J* 7.3 Hz, 2- and 8-H), 7.14 (2 H, diffuse t, *J* 7.5 Hz, 4′- and 4″-H), 7.28 (2 H, t, *J* 7.3 Hz, 3- and 9-H), 7.42 (2 H, d, *J* 7.3 Hz, 4- and 10-H), 7.60 (2 H, d, *J* 7.5 Hz, 3′- and 3″-H), 7.83 (2 H, d, *J* 7.3 Hz, 1- and 7-H), 9.83* (2 H, s, NHCO × 2), and 11.07* (2 H, s, NH × 2).

Treatment of Indole (**1**) *with Toluene*-p-*sulphonic Acid in Benzene*.—A solution of toluene-*p*-sulphonic acid (monohydrate) (16.2 g) in dry benzene (330 ml) was refluxed for 1.5 h in a Dean-Stark apparatus. After addition of indole (**1**) (25.0 g), the mixed solution was refluxed for 2.5 h and basified with aqueous 5% sodium hydrogen carbonate. Chloroform including a small quantity of methanol was then added. Insoluble material was isolated from the two-layer solution by filtration. The chloroform solution, including the 2,3′-trimer[1] (**2**) and recovered indole (**1**) (as reported in the preceding paper) were removed. The aqueous solution was extracted with ethyl acetate. The organic layer was dried (K_2CO_3) and evaporated to dryness under reduced pressure. The residue was combined with the foregoing insoluble material. Washing with hot acetone gave pale yellow prisms (1.05 g), m.p. >300 °C, identical with a sample of the tetramer (**19**) obtained by treatment of indole (**1**) with toluene-*p*-sulphonic acid in Dowtherm A.[9]

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